Atomic Absorption, Theory

Albert Kh Gilmutdinov, Kazan State University, Russia

This article is reproduced from the previous edition, volume 1, pp 33–42, © 1999, Elsevier Ltd.

Symbols

a_e	damping constant for emission lines
a	the linear dimension of the area occupied by the sample on the atomizer surface
A	absorbance
b	width of monochromator entrance slit
c(liq)	concentration of analyte in solution
c	velocity of light
D	analyte diffusion coefficient
e	charge of electron
E	activation energy
f	oscillator strength
h	height of monochromator entrance slit
$J(\lambda)$	spectral profile
$k(\lambda)$	absorption profile
l	length of absorbing layer
L	tube length
m	mass of electron
M	molecular weight of the analyte
M_A	molecular weight of analyte
M_p	molecular weight of perturbers
n_o	number density of absorbing atoms in the ground state
N	number of analyte atoms
N(g)	number of free atoms in an atomizer volume
N_0	total number of atoms in the deposited sample
N_P	number density of perturbers
$N(t)$	number of analyte atoms in the atomizer volume
R	gas constant
$R(t, t')$	removal function
$S(t')$	supply function
t	time analyte atom present in atomizer volume
t'	time of vaporization
T	absolute temperature
$T(t)$	time-dependent atomizer temperature
α	ratio of the Doppler width of the emission to the absorption line
$\Delta\nu_D$	width of Doppler-broadened atomic line
$\Delta\nu_L$	width of Lorentzian-broadened atomic line
$\varepsilon(\lambda)$	scattering coefficient
λ	wavelength
$\mu(\lambda)$	wavelength-dependent attenuation coefficient
ν	frequency factor
σ	collisional cross section
τ	mean residence time
Φ	transmitted radiant flux
Φ_0	incident radiant flux
ω	frequency (dimensionless)

Atomic absorption spectroscopy (AAS) is a technique for quantitative determination of metals and metalloids by conversion of a sample to atomic vapour and measurement of absorption at a wavelength specific to the element of interest. Owing to high sensitivity and selectivity, the technique is widely used for fundamental studies in physics and physical chemistry: measurements of oscillator strengths, diffusion coefficients of gas phase species, partial pressure of vapours, rate constants of homogeneous and heterogeneous reactions, etc. The widest application of AAS, however, is in analytical chemistry. Nowadays it is one of the most popular techniques for trace analysis of over 65 elements in practically all types of samples (environmental, biological, industrial, etc.).

The vast majority of substances to be analysed by AAS are in the condensed phase. At the same time, atomic absorption, like any other atomic spectrometry technique, can only detect free atoms that are in the gas phase. Thus, any analyte initially present in solution at a concentration c(liq) must first be transferred into the gas phase via the atomization process to produce N(g) free atoms any an atomizer volume. The analyte atoms are then detected by absorption of radiation from a primary source at a wavelength characteristic of the element resulting in an absorption signal, A. Thus, the general scheme of AAS can be presented as follows:

$$c(\text{liq}) \xrightarrow{\text{atomization}} N(\text{g}) \xrightarrow{\text{absorption}} A$$

The primary goal of the theory of AAS is to establish the relationship between the measured analytical signal, atomic absorbance, A, and the analyte concentration, c, in the sample. Theoretical description of the two stages involves entirely different sciences: theory of atomization is based on thermodynamics, kinetics and molecular